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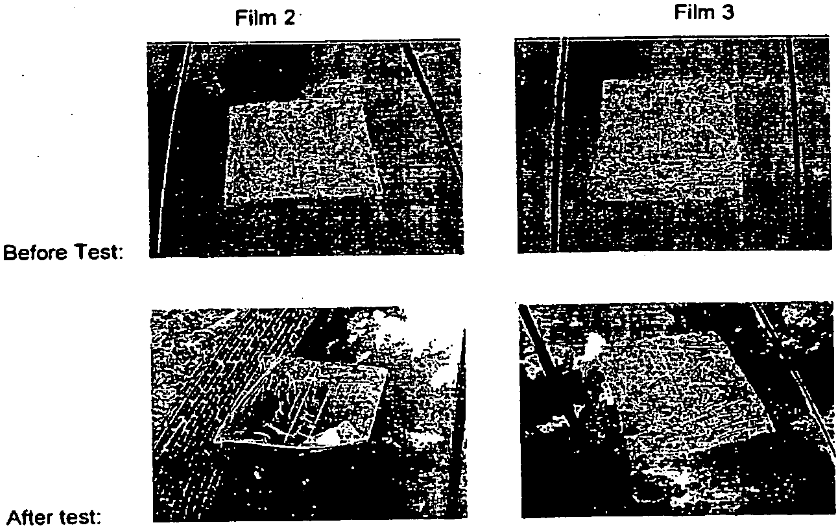
(54) Title: PROTECTIVE FILMS

Film performance on car painted bonnet/hood surface



(57) Abstract: Multilayer protective films that adhere well to many different surfaces and can be removed without leaving residues are provided. The films consist of a polyolefin backing layer(s) and an adhering layer consisting of an ethylene unsaturated ester copolymer layer containing a resin. The films have good tensile strength and stiffness at minimum thickness and can be produced by blown film and cast processes, mono and co-extrusion. The films are particularly useful for protecting automobiles during transportation and storage, a masterbatch of the resin in an ethylene polymer or copolymer to facilitate co-extrusion of the multi layer films is also provided.

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PROTECTIVE FILMS

The present invention relates to protective films and in particular to protective films that can be used to protect the surfaces of smooth articles such as glass or other transparent materials, electrical goods, displays and especially automobiles particularly during transportation and storage.

Thermoplastic films which may be applied to the automobile body for protection during transportation from manufacture to point of sale and during storage are known. In some instances, wax coatings are used. Where thermoplastic films are used, the film typically comprises a multi layer film comprising an adhering layer and a protective backing layer. The adhering layer ensures that the film will stick to an article such as an automobile under transportation and storage conditions; the protective backing layer provides the bulk of the protection and easy handling of the film when applied to the surface.

An additional requirement of the adhering layer is that the film can be readily removed from the surfaces and that removal leaves no residues.

The film must also have good strength and puncture resistance and be as thin as possible. Furthermore, the materials from which the films are made must be such that economic manufacturing techniques such as blown and cast films, either mono- or co-extrusion, which requires adequate melt strength, may be employed.

Increasingly automobiles are made from a variety of materials. Furthermore, different finishes, particularly paints, are used with different materials. For example, an automobile may contain metal body panels, rubber sealants and plastic components, such as bumpers. Metal panels are typically painted with solvent-based paint systems and plastic components with water-based paint systems. The adhesive properties of the surfaces of these materials and the paints that are used thereon differ. Accordingly, there is a need for protective films which have adequate adhesion to the various surfaces without leaving undesirable deposits on any of the surfaces after removal.

Protective films currently used consist of a polyolefin, usually polyethylene or polypropylene as backing layer and an adhering layer consisting of polyethylene or an ethylene vinyl acetate copolymer containing polyisobutylene. Whilst these films have adequate adhesion to the automobile, they cannot be removed from the automobile without leaving undesirable deposits on the surface.

A further requirement for protective films is that they may be applied at room temperature and the necessary adhesion to the surface be achieved simply by pressing the film against the surface to be protected. It will be apparent that the need to, for instance, heat the film to achieve adequate adhesion will be inconvenient when applying film to complex three-dimensional articles such as automobiles. Although films in which the adhering layer contains polyisobutylene as an adhesion enhancer can be applied at room temperature, these films tend to leave residues on the car surface when they are removed. This is thought to be due to the migration of the polyisbutylene within the polymer film.

It has been proposed in PCT Publication WO 91/06609, French Certificate of Utility 29600814, European Patent 281694 and European Patent 592913 that laminar films comprising a polyolefin backing layer and an ethylene, unsaturated ester copolymer, particularly an ethylene vinyl acetate copolymer layer as the adhering layer may be used as protective films. We have found, however, that if the vinyl acetate content of the adhering layer is sufficiently high to provide the required adhesion, the film is too weak, blocks too much, cannot be readily extruded and sticks on the reel. Furthermore, the protective films of these patents need to be applied under heat to ensure adequate adhesion.

It has been proposed in Japanese Patent publication 54-160482 that a laminated film consisting of a polyethylene base layer having a thickness up to 18 µm and an ethylene base copolymer layer having a thickness of at least 10 µm may be used to protect metal sheets such as aluminium sheets and stainless steels sheets. A petroleum resin may be incorporated in the ethylene vinyl acetate copolymer adhesive layer and an example shows an ethylene vinyl acetate copolymer layer containing 2 parts by weight of a petroleum resin. The film is used for the protection of aluminium to which it is laminated at 70°C. UK Patent application 2774729 is concerned with protective films particularly for plastic sheeting which is subsequently moulded comprising a laminated film consisting of a polyethylene base layer and an ethylene vinyl acetate copolymer adhering layer which may contain an adhesion enhancing resin.

United States Patent 5154981 is primarily concerned with stretch cling films and is concerned with the multilayer films comprising a cling layer of an ethylene unsaturated ester copolymer containing a tackifier and a polyolefin backing layer. The unsaturated ester is preferably methyl acrylate although vinyl acetate may be used. When a hydrocarbon resin tackifier is used it should have a softening point from 10°C to 25°C. Although US Patent 5154981 states that its films may be used for surface protection applications, the use of a hydrocarbon resin tackifier of such a low softening point renders the film too soft for ready processing and effective surface protection.

Japanese Patent Publication JP 04239081 is concerned with films for the protection of chemically coloured stainless steel. The films are laminar films which may consist of a polyolefin backing layer and a polyolefin or ethylene vinyl acetate copolymer adhering layer. The ethylene vinyl acetate copolymer layer may contain a hydrocarbon resin. In Example 3, which relates to such a film, the ethylene vinyl acetate copolymer contains 6% vinyl acetate. The films are thick and are applied using heat to obtain the desired adhesion.

None of the films of these patents have been commercially successful for the protection of automobiles during transport. Accordingly, there remains a need for a film, which is easily manufactured, preferably by blown or cast co-extrusion, can be reeled and unreeled, which can be applied at room temperature and which achieves sufficient adhesion to all types of surfaces. The film and its adhesion to the surface must be able to withstand the storage and transportation conditions to which it may be subjected. The film must have adequate strength, stiffness and puncture resistance, and the film must be able to be removed from the various types of surfaces without leaving undesirable deposits on the protected surface.

The present invention provides such a film.

The invention further provides a protective film comprising a polyolefin backing layer and a co-extruded ethylene polymer or copolymer adhering layer containing from 2 to 40 wt%, preferably from 2 to 30 wt %, preferably from 3 to 30 wt%, more preferably from 4 to 20 wt% and most preferably from 5 to 15 wt% of a resin of softening point above 40°C, preferably above 50°C, more preferably above 60°C, the co-extruded ethylene polymer or copolymer having a vicat softening point below 90°C.

The multilayer film preferably has a total a thickness of less than 60 μm, preferably less than 55 μm, more preferably less than 50 μm, more preferably less than 45 μm, more preferably less than 40 μm, more preferably less than 35 μm more preferably less than 30 μm, more preferably less than 25 μm more preferably less than 20 μm, a tensile strength at break (as measured by ASTM D 882 of greater than 15 MPa, preferably more than 20 MPa, more preferably more than 25 MPa and a modulus of greater than 120 MPa, preferably greater than 150 MPa, optionally greater than 170 MPa, most preferably in the range 130 to 170 MPa.

The invention further provides the use as a protective film for automobiles of a film comprising a polyolefin backing layer and a co-extruded ethylene polymer or copolymer adhering layer containing from 2 to 30 wt %, preferably from 3 to 20 wt %, more preferably from 4 to 15 wt % of a resin of softening point above 40°C, preferably above 50°C, more preferably above 60°C. The softening point (°C) of hydrocarbon resins is measured by the Ring and Ball Softening Point method according to ASTM E-28 (Revision 1996).

When the film is used for the protection of automobiles it is preferred that the film has a peel strength (as measured by D 5458) from both a water-based surface coating and a solvent-based surface coating of at least 150, preferably at least 300, more preferably at least 500, most preferably at least 600 cN per 25 mm.

In these films the choice of the polymers for the layers and the nature of the resin may be varied according to the preferred film properties. The backing layer of the multilayer film comprises a polyolefin and provides the bulk of the protection with the adhering layer of ethylene polymer or copolymer containing the hydrocarbon resin providing the adhesion to the surface to be protected.

The polymer or polymers chosen for the backing layer should provide adequate melt strength so that the multiply films may be produced by blown co-extrusion, cast co-extrusion, or any other suitable process. The backing layer is an ethylene or propylene polymer or copolymer and needs to have sufficient melt strength to enable laminar films to be produced by either blown film or casting processes. Where the laminar film is to be produced by blown film co-extrusion the ethylene or propylene polymer or copolymer should have a melt index as measured by ASTM D1238 of 0.1 to 10; preferably 1 to 7, where the film is to be produced by cast co-extrusion a melt index of 2 to 12 is preferred, more preferably 4 to 15, most preferably 5 to 12. The backing layer should be of low crystallinity, and when it is a polymer of ethylene, it may be an ethylene homopolymer or a copolymer of ethylene with other alpha olefins such as up to 30 wt % of a C_3 to C_{10} alpha olefin. The backing layer also provides the bulk of the strength and puncture resistance of the laminar films and is therefore preferably of a density of 0.915 to 0.964 g/cm^3. Ethylene polymers or copolymers prepared using metallocene catalysts are preferred. The backing layer may itself be a multi-layer structure in which one of the layers is derived from an ethylene polymer or copolymer obtained by metallocene catalysis.

The polyolefin backing layer is preferably an ethylene or propylene homopolymer or copolymer, ethylene polymers or copolymers being preferred because of their greater adhesion during co-extrusion. The density and melt index of the polyolefin, preferably polyethylene, backing layer is chosen to provide the desired strength (tensile strength), stiffness (modulus) and puncture resistance as well as the necessary melt strength when blown co-extrusion and casting is used for film production. It may be preferred to employ films containing two or more backing layers in which one type of polyolefin is used to provide a layer having a desired property such as tensile strength and/or modulus and another type of polyolefin is used to provide another desired property such as melt strength. For example, a low-density polyethylene layer may be used to provide stiffness and melt strength whereas a layer of polymer obtained by metallocene catalysis may be used to provide enhanced tensile strength and puncture resistance at low thickness.

The backing layer may contain additives such as stabilisers, antioxidants, anti-block and slip additives. Where the films are to be used for the protection of goods such as automobiles which can be parked for extended periods out of doors it is preferred that the backing layer contain a stabiliser to protect against degradation by ultra violet light such as from extended exposure to sunlight. Pigments can be added, and the films may be opaque, transparent, glossy or matt. The films may be cavitated by any of the known processes. The backing layer may also contain a resin such as a petroleum hydrocarbon resin, polyterpene resin, or a rosin ester to impart stiffness to the film, where such a resin is present it is preferred that it be present from 5 to 20% by weight and have a softening point of from 80°C to 160°C, preferably from 85°C to 150°C, more preferably from 90°C to 140°C, more preferably from 95°C to 140°C, most preferably from 100°C to 140°C. Suitable resins would include those marketed by ExxonMobil Chemical® under the designation "EMPR" (ExxonMobil Polymer Resin). Examples of the EMPR-series of resins are EMPR-100, 101, 102, 103, 104, 112, 113, 114, 124. Other resins could include hydrogenated and partially hydrogenated C9 resins such as the Arkon® P and M-series from Arakawa Chemical Company, the Regalite®R and S-series from Eastman Chemical Company, Rosin Esters such as the Sylvalite® series, Terpene-based resins such as the Sylvares® series from Arizona Chemical Company and other resins within the ranges claimed herein.

The preferred thickness of the various layers depends upon the processing ability of the polymers and the desired properties. Typically the adhering layer has a thickness of from 5 to 30 μm, preferably from 10 to 25 μm, more preferably from 10 to 20 μm and the backing layer or layers a thickness of from 10 to 50 μm, preferably between 15 to 40 μm, more preferably between 20 to 40 μm with the overall thickness of the protective film being no more than 60 μm, preferably no more than 50 μm, more preferably no more than 40 μm and no thinner than 25μm. A preferred film consists of a three layer film comprising an adhering layer of thickness at least 10 µm preferably from 10 µm to 20 µm, an intermediate layer and a backing layer both of thickness between 15 and 30 µm.

The adhering layer is co-extruded with the protective backing layer either by casting or blown film technology.

It is also preferred that the adhering layer have a melting point (as measured by ASTM D 3418) below 100°C and preferably in the range 60°C to 100°C, preferably 70°C to 95°C, more preferably 70°C to 90°C. Most preferred are the ethylene polymers and copolymers having a combination of melting point and vicat softening point disclosed herein.

The adhering layer may contain stabilisers, anti-oxidants etc. so as to improve resistance to processing and/or environmental degradation. The film may contain conventional pigments and colorants such as titanium dioxide. Calcium carbonate can also be used.

The adhering layer may be of an ethylene homopolymer or copolymer. Where it is a copolymer, it may be a copolymer of ethylene and another C_3 to C_{10} alpha olefin. Alternatively, it may be a copolymer of ethylene and an unsaturated ester. The ethylene unsaturated esters are preferred, and we prefer that the ester contain 10 to 40 wt %, preferably from 12 to 30 wt %, more preferably from 15 to 20 wt % of the unsaturated ester. For blown film operations the most preferable range is 10 wt % to 20 wt % of the unsaturated ester and for cast film operations this can be extended to 10 wt % to 30% wt % of the unsaturated ester. We have also found that providing the ethylene unsaturated ester copolymer contains from 10 to 30 wt % of the ester and has a melt index of from 0.1 to 15, preferably from 1 to 10 and more preferably between 1.5 and 3 it can be co-extruded with the backing layer without any undesirable neck-in of the polymer in the melt in the cast process or a loss of melt strength in the blown film process. The adhering layer preferably has a vicat softening point as measured by ASTM D1525 of below 90°C, preferably 40°C to 85°C, especially 60°C to 80°C.

When an ethylene unsaturated ester copolymer is used the unsaturated ester may be vinyl acetate, vinyl propionate, higher esters, C_1-C_8 acrylates, C_1-C_8 methacrylates alone or in combination. Preferred are vinyl acetate and methyl acrylate, the latter providing thermal stability. The ester content is preferably for 12 to 20 wt % and the melt index of the unsaturated ester copolymer is preferably no greater than 25, preferably no greater than 20, even more preferably no more than 15. The ethylene unsaturated ester copolymer may be made by solution polymerisation and/or high-pressure free radical process. The ester content is expressed as wt % in relation to vinyl acetate, the weight range should be adjusted on a molar basis as esters of different molecular weight are used.

Examples of commercially available ethylene vinyl acetate copolymers that may be used in the present invention include the evatane EVA copolymers supplied by Atofina, Lotryl EMA supplied by Atofina, Lotryl EMA supplied by AtofinaGreenlfex, EVA supplied by Polimeri Europe, Alcudia-PA supplied by Repsol, DuPont Elvax EVA, Escorene Ultra supplied by ExxonMobil Chemical.

Alternatively the adhering layer may be low density polyethylene ('LDPE') which includes both low and medium density polyethylene having densities of 0.910 to 0.940 g/cm^3. Low density polyethylene includes copolymers and terpolymers of ethylene. Comonomers typically include C_3-C_{10} - alpha-olefins. The ethylene content will typically be at least 80 wt % of the polyethylene co-and terpolymers. These polymers and copolymers are typically prepared by metallocene catalysed coordination polymerisation in accordance with processes well known in the polymers art. Low density polyethylenes with densities of 0.940 g/cm^3 and lower are particularly suitable for the production of the adhering layers in the films of the invention.

Examples of commercially available low density polyethylenes that may be used in this invention include Escorene LDPE from ExxonMobil Chemical, Stamylan LD from DSM, Polyethylene from Dow, LDPE from Borealis, Novex LDPE from BP, Riblene from Polimeri Euorpa, PE from Repsol Alcudia.

The high-pressure polymerisation may be effected in a conventional autoclave or tubular reactor. The polymerisation with metallocene catalysts gives a particular polymer structure depending upon the polymerisation conditions. The particular conditions are chosen having regard to the product required.

Linear low density polymers produced by metallocene catalysis (m-LLDPE) may be used to produce the backing layers of the invention. Typically, they are copolymers of ethylene with at least one alpha olefin having at least four carbon atoms e.g. 1-butene, 1-hexene, 1-octene etc. Typically, the metallocene homopolymers or copolymers are produced using mono- or bis-cyclopentadienyl transition metal catalysts in combination with an activator of alumoxane and/or a non-coordinating anion in solution, slurry, high-pressure, or gas phase. The catalyst system may be supported or unsupported and the cyclopentadienyl rings may be substituted or unsubstituted. Titanium, zirconium and hafnium are preferred transition metals. Several commercial products produced with such catalyst/activator combinations are commercially available from ExxonMobil Chemical Company under the tradenames EXCEED® and EXACT® or from Dow Chemical Company under the tradenames ENGAGE® and AFFINITY®.

The metallocene-produced copolymers described above preferably have a polydispersity less than 4 and a composition distribution breadth index (CDBI) of 50 % or more, preferably above 60%, even more preferably above 70%. In one embodiment, the CDBI is above 80%, even more preferably above 90%, even more preferably above 95%. In one embodiment, the polyethylene copolymer has a CDBI between 60 and 85%, even more preferably between 65 and 85%.

Composition Distribution Breadth Index (CDBI) is a measure of the composition distribution of monomer within the polymer chains and is measured by the procedure described in PCT publication WO 93/03093, published 18 February 1993 including that fractions having a weight average molecular weight (Mw) below 15000 are ignored when determining CDBI.

The process for producing m-LLDPE may be performed using metallocene catalysts such as those described and using a low pressure single or multiple reactor. The possible processes are: gas phase (slurry and solution) or combinations thereof. Preferably the m-LLDPE used in this invention has a density above 0.915 g/cm^3.

The resin that is incorporated into the ethylene polymer or copolymer adhering layer should be compatible with the ethylene polymer or copolymer from which the adhering layer is made so that there is little, if any, migration of the resin to the surface of the layer since this can leave deposits on the surface that has been protected after the film is removed. The resin may be selected from aliphatic hydrocarbon resins, at least partially hydrogenated aliphatic hydrocarbon resins, aliphatic/aromatic hydrocarbon resins, at least partially hydrogenated aliphatic aromatic hydrocarbon resins, cycloaliphatic hydrocarbon resins, at least partially hydrogenated cycloaliphatic resins, cycloaliphatic/aromatic hydrocarbon resins, at least partially hydrogenated cycloaliphatic/aromatic hydrocarbon resins, at least partially hydrogenated aromatic hydrocarbon resins, naturally occurring resins such as terpene resins, phenolic, terpene phenolic, rosin or rosin esters.

The softening point of the resin should be above 40°C, preferably between 40°C and 130°C, more preferably between 60°C and 130°C, preferably between 80°C and 130°C, more preferably 80°C and 120°C.

We prefer to use hydrocarbon petroleum resins or rosin esters. We prefer that the resin contain some aromaticity since this has been found to improve the compatibility with the ethylene unsaturated ester copolymer. An aromaticity of 5 to 40% as measured by ^1H NMR is preferred.

The resins may be subjected to hydrogenation by conventional means to reduce reactivity, odour, colouration and improve colour stability. The resins may be partially hydrogenated or substantially hydrogenated.

As used herein at least partially hydrogenated means that the material contains less than 90% olefinic protons, more preferably less than 75 % olefinic protons, more preferably less than 50 % olefinic protons, more preferably less than 40 % olefinic protons, more preferably less than 25 % olefinic protons, more preferably less than 15 % olefinic protons, more preferably less than 10 % olefinic protons, more preferably less than 9 % olefinic protons, more preferably less than 8 % olefinic protons, more preferably less than 7 % olefinic protons, and more preferably less than 6 % olefinic protons. As used herein, substantially hydrogenated means that the material contains less than 5% olefinic protons, more preferably less than 4 % olefinic protons, more preferably less than 3 % olefinic protons, more preferably less than 2 % olefinic protons, more preferably less than 1 % olefinic protons, more preferably less than 0.5 % olefinic protons, more preferably less than 0.1% olefinic protons, and more preferably less than 0.05% olefinic protons after hydrogenation. The degree of hydrogenation is typically conducted so as to minimize and preferably avoid hydrogenation of the aromatic bonds. The aromatic content of the resin may be adjusted to suit the polarity of the ethylene unsaturated ester copolymer.

Particularly preferred resins are those sold by ExxonMobil Chemical under the designation "EMPR" (ExxonMobil Polymer Resin) in particular EMPRs 100 to 125. The resins are chosen for maximum compatibility with the polymer, for example ahydrogenated aromatic-containing cyclopentadiene-based resin (EMPR 114) is especially useful with ethylene vinyl acetate copolymers. Alternatively, other resins described herein such as rosin esters and terpenic resins may be used. We have also found that partially hydrogenated C_9 petroleum resins are particular useful. Resins particularly suited for use as described herein include EMFR-series of resins (ExxonMobil Functional Resins) such as EMFR-100 and 101, available from ExxonMobil Chemical Company, hydrogenated and partially hydrogenated C9 resins such as the Arkon® P and M-series from Arakawa Chemical Company such as Arkon™ M90, M100, M115 and M135, the Regalite® R and S-series, Eastotac™ resins, Piccotac™ C_5/C_9 resins, and Regalrez™ aromatic from Eastman Chemical Company, Rosin Esters such as the Sylvalite® series, Terpene-based resins such as the Sylvares® series from Arizona Chemical Company, Sylvares™ phenol modified styrene-α methyl styrene resins, styrenated terpene resins, Zonatac terpend-aromatic resins, and terpene phenolic resins available from Arizona Chemical Company, Sylvatac™ and Sylvalite™ rosin esters available from Arizona Chemical Company, Norsolene™ aliphatic aromatic resins available from Cray Valley of France, Dertophene™ terpene phenolic resins available from DRT Chemical Company, Wingtack™ ET and EXTRA available from Goodyear Chemical Company, Foral™, Pentalyn™, AND Permalyn™ rosins and rosin esters available from Eastman Chemical Company, Quintone™ acid modified C_5 resins, C_5/C_9 resins, and acid modified C_5/C_9 resins available from Nippon Zeon of Japan, and LX™ mixed aromatic/cycloaliphatic resins available from Neville Chemical Company, Clearon hydrogenated terpene aromatic resins available from Yasuhara and other resins within the ranges claimed herein. The preceding examples are illustrative only and by no means limiting.

It is also preferred that the resin be incorporated into the adhering layer by means of a masterbatch which can be mixed with the ethylene polymer or copolymer which forms the adhering layer prior to co-extrusion, generally in the feed hopper of the extruder. The masterbatch consists of the resin and a polymer, generally an ethylene polymer orcopolymer which is compatible with the ethylene polymer or copolymer used to make the adhering film. The masterbatch of the invention is typically from 20 to 70 wt % resin and from 80 to 30 wt % polymer, preferably from 20 to 60 wt % resin and from 80 to 40 wt % polymer, more preferably 30 to 60 wt % resin and 70 to 40 wt % polymer. When the adhering layer is to be made from an ethylene unsaturated ester copolymer it is preferred that the polymer in the masterbatch is also an ethylene unsaturated ester copolymer, preferably the same unsaturated ester. The ester content of the polymer used in the masterbatch may, however, be lower than that of the copolymer from which the adhering layer is made to enable easier handling of the masterbatch.

Accordingly in a further embodiment, the invention provides a masterbatch comprising from 20 to 70 wt % of a resin having a softening point above 40°C and 80 to 30 wt % of an ethylene polymer or copolymer having a vicat softening point below 90°C.

Use of the masterbatch can enable better dispersion and compatibility of the polymer and the resin in the final film. The resins and ethylene polymers andcopolymers which may be used to make the masterbatch are those described herein in relation to the adhering layer of the protective film. They may be different from the polymer to which the masterbatch is added. For example the resin may be combined with a polymer in the masterbatch and then the masterbatch may be added to a different polymer. The use of a masterbatch is often recommended to ensure good mixing of all the components. This is because the molecular weights, viscosities etc. of the resin and the polymer are very different and direct blending often results in poor mixing.

The films of the present invention may be cast films or films produced by blown co-extrusion. The latter is preferred. We have found that the use of an ethylene unsaturated ester copolymer particularly an ethylene vinyl acetate copolymer of melt index 0.1 to 20 containing 10 to 30 wt % vinyl acetate (e.g. preferably between 10 and 20 wt% for blown film) and containing between 3 and 15 wt % preferably from 5 to 10 wt % of resin together with a low density polyethylene backing layer can be readily co-extruded to produce a film of the desired properties.

We have found that these films may be applied to surfaces including both painted metal and bumper (fender) surfaces of automobiles to provide protection, e.g. during transport, by application to the surfaces at ambient temperatures (~20°C). Such application results in sufficient adhesion between the ethylene unsaturated ester copolymer layer and the surfaces to withstand transport of the vehicle at normal transportation speeds and also at speeds as high as 130 kilometres/hr over periods consistent with vehicle transport. We have also found that the films may be removed from the different surfaces of the vehicle by, for example, peeling without damaging the surface finish and without leaving undesirable deposits on the surface.

Protection of other surfaces is also covered in this invention. Consumer goods such as displays, e.g. glass, plastic, liquid crystal displays etc., white goods, acrylic surfaces, e.g. plexiglass, or on anything that needs protection against damage, e.g. scratches, impacts, before use. The invention is however particularly useful in the protection of surfaces during transport.

The present invention is illustrated by the following examples.

In these examples the following polymers and hydrocarbon resins were used.

Polymers and Hydrocarbon Resins

A) A metallocene catalysed ethylene, octene copolymer plastomer of density 0.882, melt index 1 and having a melting point of 66.6°C and a vicat softening point of 53.7°C, marked by ExxonMobil Chemical as Exact 8201.

B) An ethylene vinyl acetate copolymer of melt index 3, containing 28 wt % vinyl acetate and having a melting point of 70°C and a vicat softening point of 43°C, marketed by ExxonMobil Chemical as Escorene Ultra FL 00328.

C) An ethylene vinyl acetate copolymer of melt index 14, containing 18 wt % vinyl acetate and having a melting point of 82°C and a vicat softening point of 52°C, marketed by ExxonMobil Chemical as Escorene Ultra FL 01418

D) A low density polyethylene of melt index 0.7 and density 0.923, and having a melting point of 110°C and a vicat softening point of 96°C, marketed by ExxonMobil Chemical as ExxonMobil LD 150

E) A low density polyethylene of melt index 0.75 and density 0.9280 marketed by ExxonMobil Chemical as ExxonMobil LD 170

F) A hydrogenated cyclopentadiene resin marketed by ExxonMobil Chemical as EMPR 104 (Softening Point (SP) 125°C, Tg 75°C, Mn 360 amu)

G) A hydrogenated cyclopentadiene resin marketed by ExxonMobil Chemical as EMPR 114 (SP 118°C, Tg 68°C, Mn 330 amu)

H) An ethylene vinyl acetate copolymer of containing 18 wt % vinyl acetate of melt index 1.7, and having a melting point of 85.5°C and a vicat softening point of 62°C marketed by ExxonMobil Chemical as Escorene Ultra FL 00218

I) An ethylene vinyl acetate copolymer containing 28 wt % vinyl acetate of melt index 7 and a vicat softening point of 41.5°C marketed by ExxonMobil Chemical as Escorene Ultra FL 00728

J) A low density polyethylene of melt index 3 and density 0.9335 marketed by ExxonMobil Chemical as ExxonMobil LD 151

K) A linear low density ethylene, hexene copolymer of melt index 2.5 and density 0.918 obtained by using metallocene catalysis, marketed by ExxonMobil Chemical as Exceed 2518 CB

L) A metallocene catalysed ethylene, octene copolymers plastomer of density 0.882 melt index 3 marketed by ExxonMobil Chemical as Exact 8203.

M) A linear low density metallocene polymerised polyethylene of Melt Index 1 and density 0.918 marketed by ExxonMobil Chemical as Exceed 1018 CA.

Example 1

In order to demonstrate the adhesive properties of films that can form the adhering layers of the films of the present invention, the monolayer films set out in Table 1 were produced on a laboratory Collin cast film extruder line from the formulations set out in Table 1 with the addition of conventional anti-oxidants. They were extruded at between 150°C and 180°C and a pressure of about 35 bar with a die gap of 0.6 mm an output of 3.5 kg/hr. The adhesive or adhering force when applied to steel plates coated with a solvent-based coating and a water-based coating was measured according to ASTM-D 5458 and is shown in Table 1. The adhesive or adhering force between the protective film and the coated surface was measured in cN at the moment when the 25 mm film specimen is separating from the incline at the horizontal cling line. This line is situated at 50 % of the total distance.

Table 1

Film	Polymer Formulation	Film thickness (µm)	Adhering force (cN/25 mm) on solvent-based painted steel plate	Adhering force (cN/25 mm) on water-based painted steel plate
1	H	50	55	-
2	C	31	65	48
3	95% C+ 5% F	33	120	75
4	90% C+ 10% F	33	200	120
5	90% C+ 10% G	32	180	180

Films 2 to 5 were tested in a vehicle-driving test. The films were applied after thorough cleaning of the application areas (the bonnet/hood and top/front bumper/fender). They were applied by hand from a wound roll and smoothed by light brushing. The bonnet temperature was approximately 23°C and the bumper temperature was approximately 18°C. The test involved driving at 40 to 70 km/hr for 8 km, 120 km/hr for 2.5 km, stopping and repeating the procedure in the reverse order.

Figure 1 shows the film performances on the painted metal car bonnet. As can be seen from Figure 1 Film 2 (without the hydrocarbon resin) showed signs of peeling from the surface during the first half of the test and severe peeling at the end of the test. Films 3 (5% hydrocarbon resin) and films 4 and 5 (10% hydrocarbon resin) showed no signs of peeling after the complete test. The films were easily removed and no deposits were observed on the paint surfaces. Similar results were also observed on the painted thermoplastic bumper surface where Film 2 showed peeling similar to that on the bonnet surface. Films 3 and 4 showed no peeling at all.

Example 2

Compounds of polymer H and polymer I were made with 10 % resin G. A compound of resin G with polymer A was also made for comparison. All compounds were stabilised with conventional antioxidants.

All these compounds were co-extruded on a Collin extrusion line as cast films with polymer J and polymer K as backing layers. The nature of the backing layer and the adhering layer are set out in Table 2. The films were adhered to steel painted with a water-based acrylic paint. The adhering force to metal painted with a water-based acrylic paint, the 1% Secant modulus as measured by ASTM D 882, tensile strength as measured by ASTM 882 and elongation at break as measured by ASTM D 882 of the films were obtained and the results are included in Table 2.

Table 2

Film	Identification		Total Film Thickness (μm)	Adhering force (cN)	1 % Secant Modulus (MPa)	Tensile at Break MD (MPa)	Elongation @ Break MD (%)
	Backing Layer/s	Adhering layer					
6	26 μm polymer J	11 μm 90 % polymer H + 10% resin G	39	80	209 +/- 10	34.4 +/- 2.4	352 +/- 33
7	27 μm polymer J	12 μm 90% polymer A + 10% resin G	39	160	182 +/- 7	26.0 +/- 2.2	358 +/- 37
8	26 μm polymer J	14 μm 90% polymer I + 10% resin G	40	550	174 +/- 14	26.0 +/- 1.8	337 +/- 31
9	Intermediate layer: 19 μm polymer D, backing layer: 11 μm 90% polymer K + 10% polymer J	14 μm 90% polymer I + 10% resin G	44	625	155 +/- 2	27.8 +/- 1.6	451 +/- 28
10	26 μm polymer J	14 μm polymer I	40	200	182 +/- 7	30.4 +/- 2.3	386 +/- 41

MD = Machine Direction

Addition of the hydrocarbon resins according to the present invention therefore increases the adhesive or adhering force to these smooth surfaces. Films 8 and 9 employing polymer I containing 10% resin G as adhesive layer showed the highest adhering force.

Films 5, 7, 8 and 9 were tested on an automobile in a field test. The films were applied to the bonnet of one car and the bumper of another. The driving protocol was the same as in Example 1. The ambient temperature was 18°C throughout the test. No signs of peeling were seen for any of the films containing the hydrocarbon resins on either bonnet or bumper tests. Furthermore, as observed in Figure 3, no residue was seen on the automobile after removing the film from the bonnet. The tests on the bonnet are shown in Figure 2 and the tests on the bumper in Figure 4. The films were left on the bumper for a further 7 days during which the vehicle travelled at local urban speeds of between 50 and 100 km/hr. Films 5, 7 and 9 were removed, leaving no residue. Then the vehicle was driven for over 800km at speeds of up to 130 km/hr for several hours. The weather conditions were variable involving cloud, heavy rain and high winds and the temperature varied between 11 to 15°C. Film 8 remained on the bumper and was removed after the travel (or 10 days) after application to the car, leaving no residue.

Example 3

In order to assess adhesion of potential adhering layer films 2 to 5 and films of two pure plastomers, polymers A (Film 11) and L (Film 12) were tested in a road test.

A. *Experimental Road Test*

Test conditions:

The films were applied by hand on a warm 54°C, car body and the bumper of the car.

The car was driven for 10 minutes at 50-70 km/hr and for 10 minutes at 70-120 km/hr. The car was then stopped and the results recorded for ½ the way. The reverse journey was then performed, and the end results were recorded.

Test results:

CAR BODY

	Start	½ way	End	Conclusion
Film 2	Satisfactory adhesion	partial removal	partial removal	unsatisfactory
Film 3	Satisfactory adhesion	no removal	no removal	satisfactory
Film 11	Satisfactory adhesion	partial removal	total removal	unsatisfactory
Film 12	Satisfactory adhesion	partial removal	total removal	unsatisfactory

BUMPER

	Start	½ way	End	Conclusion
Film 2	Satisfactory adhesion	partial removal	partial removal	unsatisfactory
Film 3	Satisfactory adhesion	no removal	no removal	satisfactory
Film 4	Satisfactory adhesion	no removal	no removal	satisfactory
Film 11	Satisfactory adhesion	partial removal	total removal	unsatisfactory
Film 12	Satisfactory adhesion	partial removal	partial removal	unsatisfactory

B. Lab Testing

To simulate the adherence of the film on the car and on a bumper, a lab test was set up on a Zwick tensile testing apparatus. In this test, the film is pressed against two different steel plates one of which is coated with a water-based coating and the other is coated with a solvent based coating.

The plates are fixed at an angle of 45 degrees on a sledge (wedge) and the film is peeled off from the plates at a speed of 100 mm/min, following ASTM D 5458.

The adhering force, in cN, to separate the film from the incline at the horizontal cling line, situated at 50 % of the plate at a distance of 5 cm. Also the force at the 100% distance of the plate is measured (10cm). This value is indicative of the film performance. The results are set out in Table 3. The films containing the hydrocarbon resins all achieved higher adhering forces than the control film(s) containing no hydrocarbon resin. The best adherence was delivered by films comprising resin G.

Table 3

Film	Solvent based coating			Water based coating	
	Thickness	Adhering force (cN) At 50% distance	Adhering Force (cN) At 100% distance	Adhering force (cN) At 50% distance	Adhering force (cN)At 100% distance
2	31	65	105.3 +/- 14	48	66.4 +/- 4
3	33	120	180.0 +/- 33	75	146.3 +/- 28
4	33	200	285.6 +/- 63	120	194 +/- 16
5	32	180	323.8 +/- 63	180	287.2 +/- 48

Example 4

In order to assess both adhesion and mechanical properties of films of the present invention, the following films were produced by cast co-extrusion using the following as the adhering layer:

Polymer H plus antioxidant plus 10% Resin G
Polymer I plus antioxidant plus 10% Resin G
Polymer A plus antioxidant plus 10% Resin G

Table 4

Film	Backing layer	Intermediate layer	Adhering layer
13	8 µm 90% polymer K 10% polymer J	22 µm polymer J	14 µm 90% polymer H 10% resin G
6	26 µm polymer J		11 µm 90% polymer H 10% resin G
14	23 µm polymer J		18 µm 90% polymer H 10% resin G
9	11 µm 90% polymer K 10% polymer J	19 µm polymer J	14 µm 90% polymer I 10% resin G
8	26 µm polymer J		14 µm 90% polymer I 10% resin G
10	26 µm polymer J		14 µm polymer I
15	27 µm polymer J		12 µm 90% polymer A 10% resin G
16	27 µm polymer J		12 µm polymer A

The properties of these films were measured on the Zwick tensile apparatus and found to be as shown in Table 5.

Table 5

Film	Thickness (µm)	1% Sec Modulus in MD (MPa)	Tensile @ Break in MD (MPa)	Elongation @ Break in MD (%)
6	39	209 +/- 10 MPa	34.4 +/- 2.4 MPa	352 +/- 33%
8	40	174 +/- 14 MPa	26.0 +/- 1.8 MPa	337 +/- 31%
9	43	155 +/- 2 MPa	27.8 +/- 1.6 MPa	451 +/- 28%
10	42	182 +/- 7 MPa	30.4 +/- 2.3 MPa	386 +/- 41%
11	40	182 +/- 7 MPa	26.0 +/- 2.2 MPa	358 +/- 37%

The films were adhered to water-based acrylic-coated steel. The adhering force of various film was measured on steel coated with a water based acrylic coating by peeling at 100 mm/minute and found to be as shown in Table 6. The adhering force was measured immediately after application, 24 hours after application and in the case of film 6 48 hours after application.

Table 6

Film	Thickness (µm)	**Adhering force (cN)** At 50% distance	**Adhering force (cN)** At full distance
8	40	525	787 +/- 132
9	44	525	735 +/- 47
10	40	100	157 +/- 42
11	39	140	219 +/- 26
16	39	80	102 +/- 7
After 24 hr			
8	40	550	778 +/- 160
9	44	625	910 +/- 50
10	40	200	240 +/- 13
11	39	160	277.6 +/- 58
16	39	80	120 +/- 12
After 48 Hr			
9	38	55	90.4 +/- 18
Reference:			
5	32	340	455 +/-

Table 6 illustrates that modifying the adhering layer with resin G improves the adhering force over the control film, which does not contain hydrocarbon resin.

Comparative Example 6

Two resin free co-extruded films were blown to provide the following films:

Film 17:	Polymer A (12 µm) (as the adhering layer)/ 90% polymer M 10% of polymer D (28 µm)
Film 18:	Polymer B (12 µm) (as the adhering layer)/ 90% polymer M containing 10% of polymer D and polymer E (32 µm)

The films were applied to automobiles and tested in a field test: at 40/50 km/hr both films adhered satisfactorily to the car, however at 70 km/hr both films were blown off the car, especially from the bumper.

CLAIMS

1. The use for the protection of automobiles of a multilayer protective film comprisingan adhering layer and a co-extruded backing layer wherein the backing layer comprises a polyolefin and the adhering layer is of an ethylene polymer or copolymer containing from 2 to 40 wt % of a resin having a softening point above 40°C.

2. The use according to Claim 1 in which the adhering layer contains from 2 to 30 wt % of the resin.

3. The use according to any of the preceding Claims of a film in which the ethylene polymer or copolymer of the adhering layer has a vicat softening point below 90°C.

4. The use according to any of the preceding Claims of a film produced by blown co-extrusion.

5. The use according to any of Claims 1 to 3 of a film produced by cast co-extrusion.

6. The use according to any of the preceding Claims of a film in which the backing layer is derived from a polymer of melt index 0.1 to 10.

7. The use according to any of the preceding Claims of a film in which the backing layer is derived from a polymer of melt index 2 to 12.

8. The use according to any of the preceding Claims of a film in which the backing layer is derived from a polymer or copolymer of ethylene of density 0.915 to 0.964.

9. The use according to any of the preceding Claims of a film in which the backing layer is derived from a polymer produced by metallocene catalysed polymerisation.

10. The use according to any of the preceding Claims of a film wherein the adhering layer comprises an ethylene-C_3-C_{10} alpha olefin copolymer.

11. The use according to any of the preceding Claims of a film in which the adhering layer is derived from a copolymer of ethylene and an unsaturated ester.

12. The use according to Claim 11 of a film in which the copolymer of ethylene and the

unsaturated ester is a copolymer of ethylene and vinyl acetate.

13. The use according to Claim 12 of a film in which the copolymer of ethylene and vinyl acetate contains from 2 to 30 wt % vinyl acetate.

14. The use according to any of the preceding Claims of a film which has an overall thickness of less than 60 μm.

15. The use according to any of the preceding Claims of a film having a tensile strength at break of greater than 15 mPa.

16. The use according to any of the preceding Claims of a film having a modulus greater than 120 mPa.

17. The use according to any of the preceding Claims of a film in which the adhering layer has a thickness of from 5 to 30 μm.

18. The use according to any of the preceding Claims of a film in which the backing layer or layers have a thickness of from 10 to 50 μm.

19. The use according to any of the preceding Claims of a film wherein the resin comprises an at least partially hydrogenated aromatic-containing cyclopentadiene resin.

20. A multilayer protective film comprising an adhering layer and a co-extruded backing layer wherein the backing layer is of a polyolefin and the adhering layer is of an ethylene polymer or copolymer containing from 2 to 40 wt % of a resin having a softening point above 40°C wherein the adhering layer is of an ethylene polymer or copolymer having a vicat softening point below 90°C.

21. A multiplayer protective film according to Claim 20 in which the adhering layer contains from 2 to 30 wt % of the resin.

22. A multiplayer protective film according to Claim 20 or Claim 21 in which the ethylene polymer or copolymer of the adhering layer has a vicat softening point of from 40°C to 90°C.

23. A multiplayer protective film according to any of Claims 20 to 22, in which the adhering

layer is of an ethylene polymer or copolymer having a melting point below 100°C.

24. A multiplayer protective film according to any of Claims 20 to 23, in which the adhering layer is of an ethylene polymer or copolymer having a melting point in the range 65°C to 100°C.

25. A multilayer protective film according to any of Claims 20 to 24 of a film produced by blown co-extrusion.

26. A multilayer protective film according to any of Claims 20 to 24 produced by cast co-extrusion.

27. A multilayer protective film according to Claim 25 in which the backing layer is derived from a polymer of melt index 0.1 to 10.

28. A multilayer protective film according to Claim 26 in which the backing layer is derived from a polymer of melt index 2 to 12.

29. A multilayer protective film according to any of Claims 20 to 28 in which the backing layer is derived from a polymer or copolymer of ethylene of density from 0.915 to 0.964.

30. A multilayer protective film according to any of Claims 20 to 29 in which the backing layer is derived from a polymer produced by metallocene catalysed polymerisation.

31. A multilayer protective film according to any of Claims 20 to 30 wherein the adhering layer comprises an ethylene-C_3-C_{10} alpha olefin copolymer.

32. A multilayer protective film according to any of Claims 20 to 30 in which the adhering layer is derived from a copolymer of ethylene and an unsaturated ester.

33. A multilayer protective film according to Claim 32 in which the copolymer of ethylene and the unsaturated ester is a copolymer of ethylene and vinyl acetate.

34. A multilayer protective film according to Claim 33 in which the copolymer of ethylene and vinyl acetate contains from 2 to 30 wt % vinyl acetate.

35. A multilayer protective film according to any of Claims 20 to 34 having an overall

thickness of less than 60 µm.

36. A multilayer protective film according to any of Claims 20 to 35 having a tensile strength at break of greater than 15 mPa.

37. A multilayer protective film according to any of Claims 20 to 36 having a modulus greater than 120 mPa.

38. A multilayer protective film according to any of Claims 20 to 37 in which the adhering layer has a thickness of from 5 to 30 µm.

39. A multilayer protective film according to any of Claims 20 to 38 in which the backing layer or layers have a thickness of from 10 to 50 µm.

40. A multilayer protective film according to any of Claims 20 to 39 wherein the resin comprises an at least partially hydrogenated aromatic-containing cyclopentadiene resin.

41. A masterbatch comprising from 20 to 70 wt % of a resin having a softening point above 40°C and 80 to 30 wt % of an ethylene polymer or copolymer having a vicat softening point below 90°C.

42. A masterbatch according to Claim 42 in which the resin has a softening point of 80°C to 130°C.

43. A masterbatch according to Claim 41 or Claim 42 in which the ethylene polymer or copolymer has a vicat softening point in the range 50°C to 90°C.

44. A masterbatch according to any of Claims 41 to 43 in which the ethylene polymer or copolymer has a melting point below 100°C.

45. A masterbatch according to Claim 44 in which the ethylene polymer or copolymer has a melting point in the range of 65°C to 100°C.

46. A masterbatch according to any of Claims 41 to 45 in which the ethylene polymer or copolymer is a copolymer of ethylene and an unsaturated ester.

47. A masterbatch according to Claim 46 in which the unsaturated ester is vinyl acetate.

48. A masterbatch according to any of Claims 41 to 47 in which the resin is an aromatic containing cyclopentadiene resin.

49. A masterbatch according to any of Claims 41 to 47 in which the resin is a C_9 aromatic resin.

50. A masterbatch according to Claim 48 or Claim 49 in which the resin is at least partially hydrogenated.

51. The use of a masterbatch according to any of Claims 41 to 50 to produce a protective film.

52. A process for the production of multilayer films comprising coextruding a backing layer and an adhering layer wherein the backing layer comprises a polyolefin and the adhering layer is of an ethylene polymer of copolymer containing from 2 to 40 wt % of a resin having a softening point above 40°C wherein the adhering layer is obtained by blending under high shear conditions an ethylene polymer or copolymer and the resin to form a concentrate containing from 20 to 70 wt % of the resin and subsequently blending the concentrate with the ethylene polymer or copolymer of the adhering layer and coextruding the resultant blend with the backing layer to form a multilayer film.

53. A process according to Claim 52 in which the concentrate and ethylene polymer and copolymer are blended so that the adhering layer contains from 2 to 30 wt % of the resin.

54. A process according to Claim 52 or Claim 53 in which the ethylene polymer or copolymer of the adhering layer has a vicat softening point of from 40°C to 90°C.

55. A process according to any of Claims 52 to 54, in which the adhering layer is of an ethylene polymer or copolymer having a melting point below 100°C.

56. A process according to any of Claims 52 to 55 in which the backing layer is derived from a polymer of melt index 0.1 to 10.

57. A process according to any of Claims 52 to 56 in which the backing layer is derived

from a polymer or copolymer of ethylene of density from 0.915 to 0.964.

58. A process according to any of Claims 52 to 57 in which the backing layer is derived from a polymer produced by metallocene catalysed polymerisation.

59. A process according to any of Claims 52 to 58 wherein the adhering layer comprises an ethylene-C_3-C_{10} alpha olefin copolymer.

60. A process according to any of Claims 52 to 58 in which the adhering layer is derived from a copolymer of ethylene and an unsaturated ester.

61. A process according to Claim 60 in which the copolymer of ethylene and the unsaturated ester is a copolymer of ethylene and vinyl acetate.

62. A process according to any of Claims 52 to 61 wherein the resin comprises an at least partially hydrogenated aromatic-containing cyclopentadiene resin.

63. A process according to any of Claims 52 to 62 in which an intermediate layer is coextruded between the adhering layer and the backing layer.

AMENDED CLAIMS

[received by the International Bureau on 25 February 2003 (25.02.03);
new pages 19-24 in replacement of current pages 19-24. (6 pages)]

1. The use for the protection of automobiles of a multilayer protective film comprising an adhering layer and at least one co-extruded backing layer wherein the backing layer comprises a polyolefin and the adhering layer comprises: (i) an ethylene polymer or copolymer having a vicat softening point of 40-90°C; and (ii) 2 to 40 wt % of a resin having a softening point above 40°C.

2. The use according to claim 1 wherein the adhering layer contains from 2 to 30 wt % of the resin.

3. The use according to any of the preceding claims wherein the film is produced by blown co-extrusion.

4. The use according to any of claims 1 or 2 wherein the film is produced by cast co-extrusion.

5. The use according to claim 3 wherein the backing layer is derived from a polymer having a melt index of 0.1 to 10.

6. The use according to claim 4 wherein the backing layer is derived from a polymer having a melt index of 2 to 12.

7. The use according to any of the preceding claims wherein the backing layer is derived from a polymer or copolymer of ethylene having a density of 0.915 to 0.964.

8. The use according to any of the preceding claims wherein the backing layer is derived from a polymer produced by metallocene catalysed polymerisation.

9. The use according to any of the preceding claims wherein the adhering layer comprises a copolymer of ethylene and a C_3-C_{10} α-olefin.

10. The use according to any of the preceding claims wherein the adhering layer is derived from a copolymer of ethylene and an unsaturated ester.

11. The use according to claim 10 wherein the unsaturated ester is vinyl acetate.

12. The use according to claim 11 wherein the copolymer contains 2 to 30 wt % vinyl acetate.

13. The use according to claim 11 wherein the copolymer contains 10 to 40 wt % vinyl acetate.

14. The use according to any of the preceding claims wherein the film has an overall thickness less than 60 µm.

15. The use according to any of the preceding claims wherein the film has a tensile strength at break greater than 15 mPa.

16. The use according to any of the preceding claims having a modulus greater than 120 mPa.

17. The use according to any of the preceding claims wherein the adhering layer has a thickness of 5 to 30 µm.

18. The use according to any of the preceding claims wherein the backing layer or layers have a thickness of 10 to 50 µm.

19. The use according to any of the preceding claims of a film wherein the resin comprises an at least partially hydrogenated aromatic-containing cyclopentadiene resin.

20. A multilayer protective film comprising an adhering layer and at least one co-extruded backing layer wherein the backing layer comprises a polyolefin and the adhering layer comprises (i) an ethylene polymer or copolymer having a vicat softening point of 40-90°C, and (ii) 2 to 40 wt % of a resin having a softening point above 40°C.

21. A multilayer protective film according to claim 20 wherein the adhering layer contains 2 to 30 wt % of the resin.

AMENDED SHEET (ARTICLE 19)

22. A multilayer protective film according to claims 20 or 21 wherein the ethylene polymer or copolymer of the adhering layer has a vicat softening point of 40-85°C.

23. A multilayer protective film according to any of claims 20 to 22 wherein the adhering layer comprises an ethylene polymer or copolymer having a melting point below 100°C.

24. A multilayer protective film according to claim 23 wherein the adhering layer comprises an ethylene polymer or copolymer having a melting point of 65-100°C.

25. A multilayer protective film according to any of claims 20 to 24 wherein the film is produced by blown co-extrusion.

26. A multilayer protective film according to any of claims 20 to 24 wherein the film is produced by cast co-extrusion.

27. A multilayer protective film according to claim 25 wherein the backing layer is derived from a polymer of melt index 0.1 to 10.

28. A multilayer protective film according to claim 26 wherein the backing layer is derived from a polymer of melt index 2 to 12.

29. A multilayer protective film according to any of claims 20 to 28 wherein the backing layer is derived from a polymer or copolymer of ethylene of density from 0.915 to 0.964.

30. A multilayer protective film according to any of claims 20 to 29 wherein the backing layer is derived from a polymer produced by metallocene catalysed polymerisation.

31. A multilayer protective film according to any of claims 20 to 30 wherein the adhering layer comprises a copolymer of ethylene and a C_3-C_{10} α-olefin.

32. A multilayer protective film according to any of claims 20 to 30 wherein the adhering layer is derived from a copolymer of ethylene and an unsaturated ester.

33. A multilayer protective film according to claim 32 wherein the unsaturated ester is vinyl acetate.

34. A multilayer protective film according to claim 33 wherein the copolymer contains from 2 to 30 wt % vinyl acetate.

35. A multilayer protective film according to any of claims 20 to 34 having an overall thickness of less than 60 µm.

36. A multilayer protective film according to any of claims 20 to 35 having a tensile strength at break of greater than 15 mPa.

37. A multilayer protective film according to any of claims 20 to 36 having a modulus greater than 120 mPa.

38. A multilayer protective film according to any of claims 20 to 37 wherein the adhering layer has a thickness of from 5 to 30 µm.

39. A multilayer protective film according to any of claims 20 to 38 wherein the backing layer or layers have a thickness of from 10 to 50 µm.

40. A multilayer protective film according to any of claims 20 to 39 wherein the resin comprises an at least partially hydrogenated aromatic-containing cyclopentadiene resin.

41. A masterbatch comprising from 20 to 70 wt % of a resin having a softening point above 40°C and 80 to 30 wt % of an ethylene polymer or copolymer having a vicat softening point below 90°C.

42. A masterbatch according to claim 42 wherein the resin has a softening point of 80°C to 130°C.

43. A masterbatch according to claim 41 or claim 42 wherein the ethylene polymer or copolymer has a vicat softening point in the range 40°C to 90°C.

44. A masterbatch according to any of claims 41 to 43 wherein the ethylene polymer or copolymer has a melting point below 100°C.

45. A masterbatch according to claim 44 wherein the ethylene polymer or copolymer has a melting point of 65-100°C.

46. A masterbatch according to any of claims 41 to 45 wherein the ethylene polymer or copolymer is a copolymer of ethylene and an unsaturated ester.

47. A masterbatch according to claim 46 wherein the unsaturated ester is vinyl acetate.

48. A masterbatch according to any of claims 41 to 47 wherein the resin is an aromatic-containing cyclopentadiene resin.

49. A masterbatch according to any of claims 41 to 47 wherein the resin is a C_9 aromatic resin.

50. A masterbatch according to claim 48 or claim 49 wherein the resin is at least partially hydrogenated.

51. The use of a masterbatch according to any of claims 41 to 50 to produce a protective film.

52. A process for the production of multilayer films comprising:

(a) coextruding a backing layer and an adhering layer wherein the backing layer comprises a polyolefin and the adhering layer comprises

(i) an ethylene polymer of copolymer having a vicat softening point of 40-90°C, and

(ii) 2 to 40 wt % of a resin having a softening point above 40°C,

wherein the adhering layer is obtained by blending under high shear conditions an ethylene polymer or copolymer and the resin to form a concentrate containing from 20 to 70 wt % of the resin;

(b) subsequently blending the concentrate with the ethylene polymer or copolymer of the adhering layer; and

(c) coextruding the resultant blend with the backing layer to form a multilayer film.

53. A process according to claim 52 wherein the concentrate and ethylene polymer and copolymer are blended so that the adhering layer contains from 2 to 30 wt % of the resin.

54. A process according to claim 52 or claim 53 wherein the ethylene polymer or copolymer of the adhering layer has a vicat softening point of from 40°C to 85°C.

55. A process according to any of claims 52 to 54, wherein the adhering layer comprises an ethylene polymer or copolymer having a melting point below 100°C.

56. A process according to any of claims 52 to 55 wherein the backing layer is derived from a polymer having a melt index of 0.1 to 10.

57. A process according to any of claims 52 to 56 wherein the backing layer is derived from a polymer or copolymer of ethylene having a density of 0.915 to 0.964.

58. A process according to any of claims 52 to 57 wherein the backing layer is derived from a polymer produced by metallocene catalysed polymerisation.

59. A process according to any of claims 52 to 58 wherein the adhering layer comprises a copolymer of ethylene and a C_3-C_{10} α-olefin.

60. A process according to any of claims 52 to 58 wherein the adhering layer is derived from a copolymer of ethylene and an unsaturated ester.

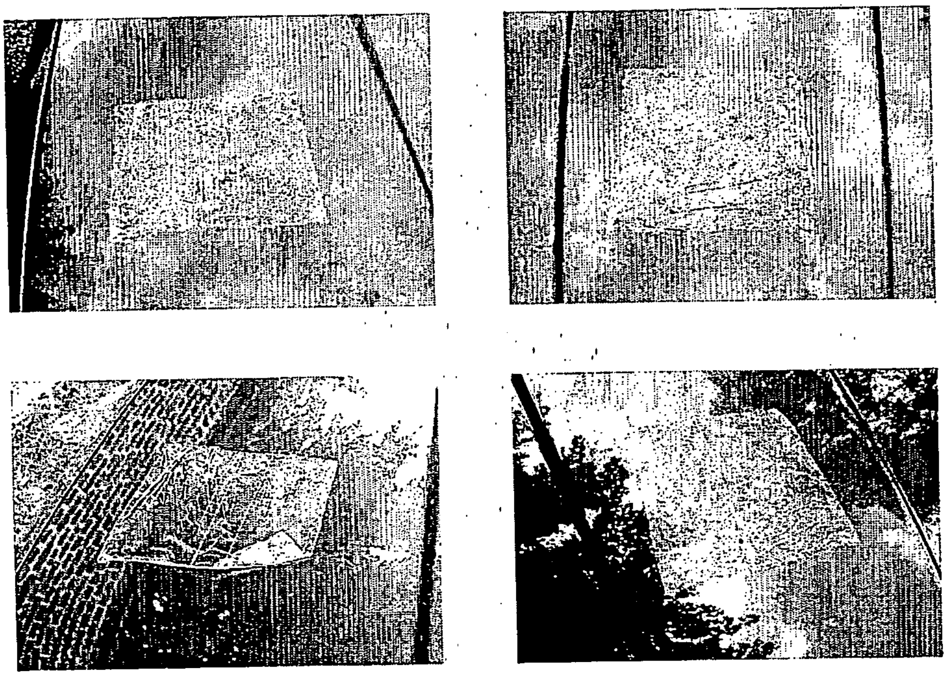
61. A process according to claim 60 wherein the unsaturated ester is vinyl acetate.

62. A process according to any of claims 52 to 61 wherein the resin comprises an at least partially hydrogenated aromatic-containing cyclopentadiene resin.

63. A process according to any of claims 52 to 62 wherein an intermediate layer is coextruded between the adhering layer and the backing layer.

Figure 1

Film performance on car painted bonnet/hood surface



Film 2

Film 3

Before Test:

After test:

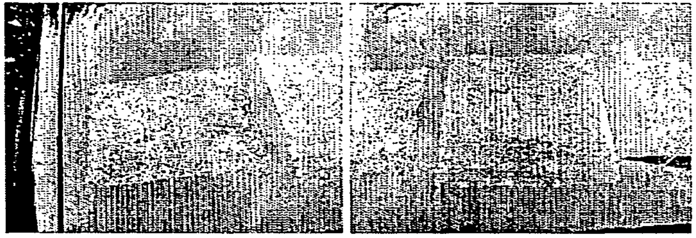
NSDOCID: <WO 03039860A1 | >

Figure 2

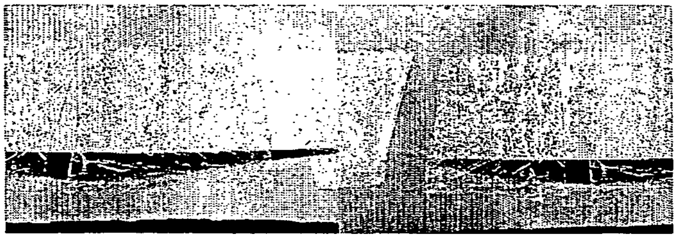
Film performance on car painted bonnet/hood surface

Before test:

Film 5 Film 9



Film 8 Film 7



After test:

Film 5 Film 9

Film 8 Film 7

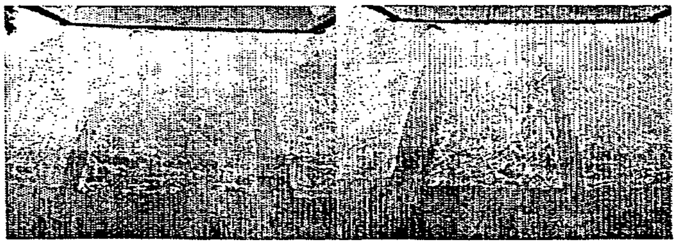


Figure 3

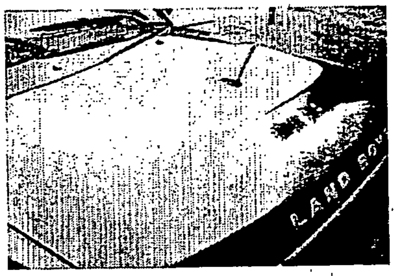
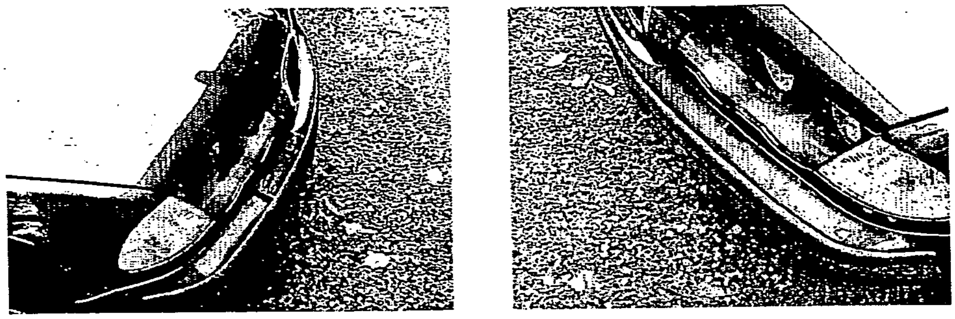


Figure 4

Film performance on car painted bumper/fender surface

Film 5 and Film 9

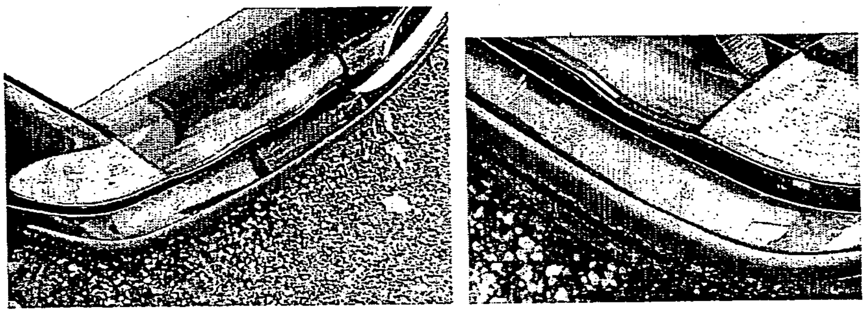
Film 7 and 8



Before test:

Film 5 and Film 9

Film 7 and 8



After test:

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 02/33487

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B32B27/08 C09J7/02 C08L23/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09J C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search 13 January 2003	Date of mailing of the international search report 23/01/2003
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer De Jonge, S

INTERNATIONAL SEARCH REPORT

Interna[illegible] Application No
PCT/US 02/33487

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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X	US 5 154 981 A (BRANT PATRICK ET AL) 13 October 1992 (1992-10-13) cited in the application column 7, line 34 -column 8, line 34; claims; examples	20-24, 27-29, 31-51
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